a 2-hr period with ice-bath cooling. The product mixture was then allowed to stand overnight at room temperature. The mixture was hydrolyzed by adding to a mixture of ice and water, and the resulting mixture was neutralized with saturated sodium carbonate solution. The organic product was extracted with ether, washed with water, and finally dried with anhydrous magnesium sulfate. The ether was removed under reduced pressure, yielding crude 4-bromo-1,5-octadiene (**14**) as a yellow, lachrymatory, unstable liquid (99 g, 87% crude yield).

Crude 4-bromo-1,5-octadiene (99 g, 0.52 mol), *N*,*N*-dimethylbenzylamine (94.5 g, 0.70 mol), and toluene (800 ml) were mixed and allowed to stand overnight at room temperature. The mixture was then heated on a steam cone for 8 hr to complete formation of the quaternary salt, which was then removed by filtration as a crude brown semisolid (126 g, 75%). A small portion was recrystallized from EtOH–EtOAc, mp 141–142°. The remainder of the crude product was dissolved in 600 ml of water, and the aqueous solution was extracted several times with ether to remove suspended organic impurities. The aqueous solution of the salt was then heated to boiling to remove any dissolved ether, yielding a clear yellow solution of benzyldimethyl-4-(1,5-octadienyl)ammonium bromide (**15**).

1,3,5-Octatriene (**11**).—The above aqueous solution of **15** was added dropwise to a solution of sodium hydroxide (128 g in 800 ml of water) which was undergoing distillation. The organic product was extracted from the distillate with ether, and the ether solution was washed several times with 3 *N* HCl, followed by several water washings. The ether solution was dried with anhydrous magnesium sulfate, filtered, and distilled at reduced pressure, yielding **11** (12 g, 28%): bp 52–53° (23 mm); n^{23}D 1.5200; λ_{max}^{iso} 274, 263, 254 nm ($\epsilon \times 10^{-4}$ 3.10, 3.90. 290) [lit.[30] n^{26}D 1.5170; λ_{max} 274, 264, 254 nm ($\epsilon_{max} \times 10^{-4}$ 2.72, 3.46, 2.76)]; nmr τ 9.0 (t, 3 H, J = 7 Hz, methyl), 7.6–8.2 (q, 2 H, J = 7 Hz, allylic methylene), 2.8–5.2 (m, 7 H, vinyl). Glpc analysis indicated a mixture of geometric isomers composed of 68% trans,trans- and 32% cis,trans configurations.

2-Methyl-1,3,5-heptatriene (**4**).—*trans*-2-Methyl-1,5-heptadien-4-ol[31] (141 g, 1.12 mol) in 200 ml of anhydrous ether was allowed to react with phosphorus tribromide (120 g, 0.42 mol) in a manner similar to that described above for 4-bromo-1,5-octadiene, yielding 4-bromo-2-methyl-1,5-heptadiene (187 g, 99%) as a crude lachrymatory liquid. The crude bromide (0.99 mol), in 100 ml of DMSO, was added dropwise to a solution of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (1.05 mol) and the reaction mixture was worked up as we have recently described.[32] 2-Methyl-1,3,5-heptatriene (**4**) (32 g, 30%) was obtained as a mixture of geometric isomers composed of 85% *trans,trans*- and 15% *cis,trans*-**4**: bp 68–70° (25 mm); n^{25}D 1.5263; λ_{max} 272, 262, 252 nm ($\epsilon \times 10^{-4}$ 3.84, 4.68, 3.48); nmr τ 8.0–8.3 (m, 6 H, 2 CH_3C=), 5.05 (s, 2 H, CH_2=), 3.6–4.6 (m, 4 H, CH=CH) (lit.[32] identical with those above).

Thermolysis of 1,3,5-Octatriene, a Typical Run.—1,3,5-Octatriene (2.0 g) was thermolyzed in a manner identical with that described for **1**. At 425° 1.9 g of product was obtained (95% recovery) and submitted to glpc analysis, yielding the following product distribution: 5-ethyl-1,3-cyclohexadiene, 18.6%; 1-ethyl-1,3-cyclohexadiene, 26.2%; *trans,trans*-**11**, 55.0%; *cis,trans*-**11**, 0.2%. No other products were detected. Assignment of structure to the thermolysis products was accomplished by comparison of uv, nmr, and glpc retention times to those of authentic samples.

Thermolysis of 2-Methyl-1,3,5-heptatriene, a Typical Run.—2-Methyl-1,3,5-heptatriene (5.0 g) was thermolyzed in a manner identical to that described for **1**. The results are tabulated in Table III. At 425° 4.2 g of product was obtained (84% recovery) and submitted to glpc analysis.

Registry No.—**1**, 33482-80-3; *trans,trans*-**4**, 17679-94-6; *cis,trans*-**4**, 18304-16-0; **5**, 1453-17-4; **6**, 2050-32-0; **7**, 4573-05-1; *trans,trans*-**11**, 33580-04-0; *cis,trans*-**11**, 33580-05-1; **12**, 1073-13-8; **12** tosylhydrazone, 21195-63-1; **13**, 33580-07-3; **15**, 33580-08-4.

(30) K. Alder and H. von Brachel, *Justus Liebigs Ann. Chem.*, **608**, 195 (1956).

(31) Chemical Samples Co., Columbus, Ohio.

(32) C. Spangler, R. Eichen, K. Silver, and B. Butzlaff, *J. Org. Chem.*, **36**, 1695 (1971).

Reactions of Dienamines and Dienol Ethers

MARTIN E. KUEHNE* AND GERALD DIVINCENZO

Department of Chemistry, University of Vermont, Burlington, Vermont 05401

Received September 10, 1971

The bicyclic morpholine dienamines I and II derived from 4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone and the corresponding 4a-methyl compound reacted on the nitrogen-substituted double bond with a nitrile oxide, an acyl azide, diethyl diazodicarboxylate, and the methylene-donating reagent methylene iodide and diethylzinc. The latter reagent reacted preferentially at the alternative double bond of the corresponding enol ether. Reactions of the dienamines with a sulfonimide occurred at both double bonds while phenylsulfene was regiospecific for the terminal double bond of the activated dienamine systems.

Conjugated dienes, which are substituted by electron-donating or -withdrawing substituents can be expected to react at more than one position. Prediction of a specific preferred reaction site should be governed by considerations of location of maximum charge density in the ground state of the diene, optimum electronic stabilization in the reaction transition state, as well as steric barriers at either reaction stage. Since these factors may or may not act in the same direction and will be differently weighted for different reactions, one would anticipate variations in the preferred position of attack on conjugated dienes. Indeed, lacking suitable analogies, one may find it difficult to predict a preferred reaction site with strong conviction for a given diene and reagent. The present study was undertaken to extend information on such reactions.

It has previously been found that fluorination of dienamine derivatives[1-6] of Δ^4-3-keto steroids leads to 4-fluoro products, whereas the corresponding enol ether[6,7] and enol acetate[8,9] derivatives gave predominantly 6-fluoro products. Halogenation of dienol ethers with *N*-halosuccinimides also led to substitution

(1) R. Joly, J. Warnant, A. Guillemette, and B. Goffinet (Roussel-UCLAF), German Patent 11 59 434 (1960); *Chem. Abstr.*, **61**, 1921 (1964).

(2) R. Joly and J. Warnant, *Bull. Soc. Chim. Fr.*, 569 (1961).

(3) S. Nakanishi, R. L. Morgan, and E. V. Jensen, *Chem. Ind. (London)*, 1136 (1960).

(4) D. H. R. Barton, L. S. Godinho, R. H. Hesse, and M. M. Pechet, *Chem. Commun.*, 804 (1968).

(5) S. Nakanishi, *Steroids*, **2**, 765 (1963).

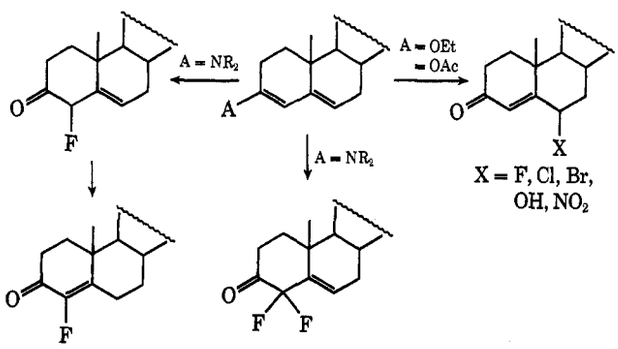
(6) J. Magerlein, J. E. Pike, R. W. Jackson, G. E. Vanderberg, and F. Kagan, *J. Org. Chem.*, **29**, 2982 (1964).

(7) S. Nakanishi, K. Morita, and E. Jensen, *J. Amer. Chem. Soc.*, **81**, 5259 (1959).

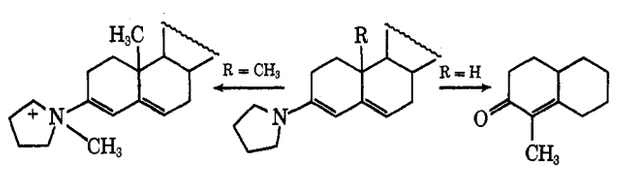
(8) Y. Osawa and M. Neeman, *J. Org. Chem.*, **32**, 3055 (1967).

(9) H. J. Ringold, E. Batres, A. Bowers, J. Edwards, and J. Zderic, *J. Amer. Chem. Soc.*, **81**, 3485 (1959).

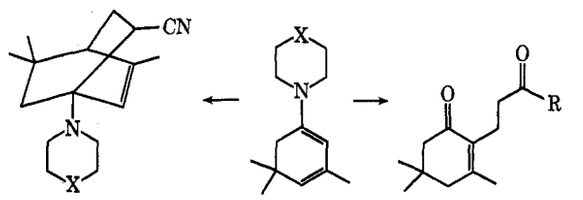
at the terminal double bond.[9] This position of substitution was again found in hydroxylations of dienol ethers[10] and dienol acetates[11] with monoperphthalic[10] and *m*-chloroperbenzoic[11] acids, as well as in an enol acetate nitration with fuming nitric acid.[12]



While methylation of the pyrrolidine enamine derivative of testosterone has been reported to take place on nitrogen,[13] carbon methylation was achieved in a corresponding octalone derivative[14,15] where steric shielding by an angular methyl group is not present. In this example alkylation was found at the double bond nearest the nitrogen. This position of reaction was also realized on alkylations with 3-methoxybenzyl bromide,[16] 1,3-dichloro-2-butene,[18] ethyl acrylate,[19] acryloyl chloride,[20] methyl vinyl sulfone,[21] and dichlorocarbene (with ring expansion).[22]

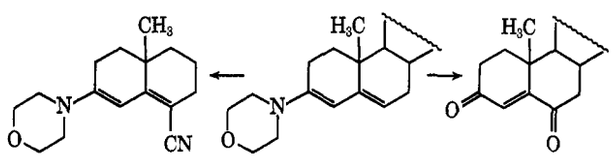


On the other hand, analogous dienol ethers were found to react with tetrabromomethane or bromotrichloromethane to give dihalomethylene substitution at the end of the activated diene system.[23] Additions of α,β-unsaturated nitriles,[24] esters,[24] and ketones,[24,25] and of diketene[26] to endocyclic cisoid dienamines provided examples of additions β to the amine nitrogen

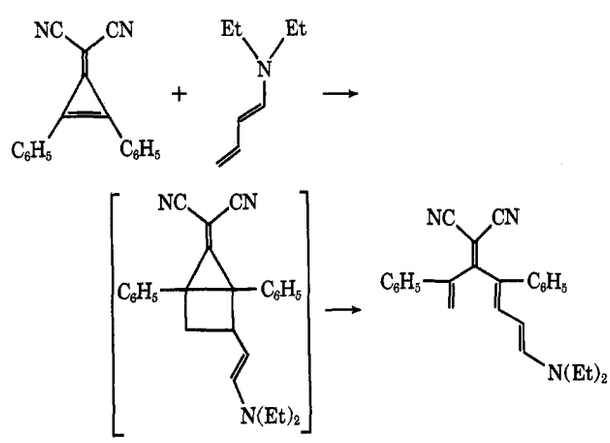


as well as the Diels–Alder products also observed with acyclic dienamines.[27-31]

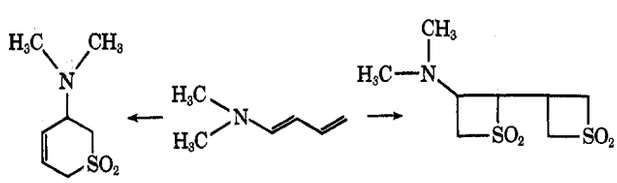
In contrast to the foregoing dienamine reactions it was found that cyanogen chloride[32] and oxygen with copper[33] react at the terminal double bond of dienamine derivatives of β-octalone systems.



Cycloaddition of 1,2-diphenyl-3-dicyanomethylenecyclopropane[34] to the terminal double bond of 1-diethylaminobutadiene led to a cyclobutane intermediate which opened to a cross-conjugated tetraene.



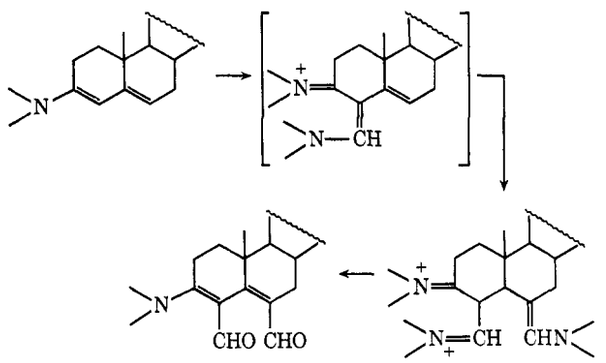
The formation of double adducts and a Diels–Alder product from sulfene and 1-dimethylaminobutadiene suggest preferred initial reaction at the terminal end of the diene system for this reaction as well.[35,36]



Disubstitution of dienamines was also found with the Vilsmeier reagent.[37] However, here an initial attack

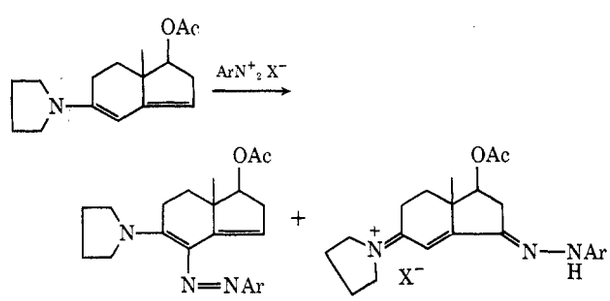
(10) J. Romo, G. Rosenkranz, C. Djerassi, and F. Sondheimer, *J. Org. Chem.*, **19**, 1509 (1954).
(11) D. N. Kirk and J. M. Wiles, *Chem. Commun.*, 518 (1970).
(12) A. Bowers, L. C. Ibanez, and H. J. Ringold, *J. Amer. Chem. Soc.*, **81**, 3707 (1959).
(13) G. Stork, R. Terrell, and J. Szmuszkovics, *ibid.*, **76**, 2029 (1954).
(14) G. Stork and G. Birnbaum, *Tetrahedron Lett.*, 313 (1961).
(15) M. Julia, S. Julia, and C. Jeanmart, *C. R. Acad. Sci., Ser. C.*, **251**, 249 (1960).
(16) U. K. Pandit, K. DeJonge, K. Erhart, and H. O. Huisman, *Tetrahedron Lett.*, 1207 (1969). The high yield of carbon alkylation in this example, analogous to the above testosterone enamine methylation, is likely due to rearrangement of an initial *N*-benzyl product at the temperature of refluxing dimethylformamide.[17]
(17) M. E. Kuehne and T. Garbacik, *J. Org. Chem.*, **35**, 1555 (1970).
(18) L. Velluz, G. Nominé, R. Bucourt, A. Pierdet, and P. Dufay, *Tetrahedron Lett.*, 127 (1961).
(19) A. A. Brizzolara, Ph.D. Thesis, Columbia University, 1960.
(20) H. F. Firrell and P. W. Hickmott, *J. Chem. Soc. C*, 2320 (1968).
(21) D. Bertin and J. Perronet, *Bull. Soc. Chim. Fr.*, 1422 (1968).
(22) U. Pandit and S. de Graaf, *Chem. Commun.*, 381 (1970).
(23) S. Liisberg, W. Godtfredsen, and S. Vangedal, *Tetrahedron*, **9**, 149 (1960).
(24) H. Nozaki, T. Yamagute, S. Ueda, and K. Kondo, *ibid.*, **24**, 1445 (1968).
(25) A. J. Birch, E. G. Hutchinson, and G. S. Rao, *Chem. Commun.*, 657 (1970).
(26) B. B. Millward, *J. Chem. Soc.*, 26 (1960).
(27) H. Leotte, *Rev. Port. Quim.*, **7**, 214 (1965); *Chem. Abstr.*, **65**, 13647 (1966).
(28) G. Opitz and H. Holtmann, *Justus Liebigs Ann. Chem.*, **684**, 79 (1965).
(29) S. Hünig and K. Kahanek, *Chem. Ber.*, **90**, 238 (1957).
(30) J. Ciabattoni and G. A. Berchtold, *J. Amer. Chem. Soc.*, **87**, 1404 (1965).
(31) J. Ciabattoni and G. A. Berchtold, *J. Org. Chem.*, **31**, 1336 (1966).
(32) M. E. Kuehne and J. A. Nelson, *ibid.*, **35**, 161 (1970).
(33) V. Van Rheenen, *Chem. Commun.*, 314 (1969).
(34) J. Ciabattoni and E. C. Nathon, *J. Amer. Chem. Soc.*, **89**, 3081 (1967).
(35) G. Opitz and F. Schweinsberg, *Angew. Chem.*, **77**, 811 (1965).
(36) L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967).
(37) R. Sciaky, U. Pallini, and A. Consonni, *Gazz. Chim. Ital.*, **96**, 1284 (1966).

on the nitrogen-substituted double bond can give rise to a new enamine which may then react with a second equivalent of the acylating agent. Diformylation of methylenecyclohexane at the methylene carbon in a Vilsmeier reaction[38] can be formulated as the analogous reaction of an initially formed dienamine.



In contrast, dienol ether derivatives of Δ^4-3-keto steroids[39,40] gave terminal acylation products (at C-6) in Vilsmeier reactions while the dienol acetate derivative of a 19-nor compound and its parent enone[41] led to equal acylation at both double bonds (C-4 and C-6).[42]

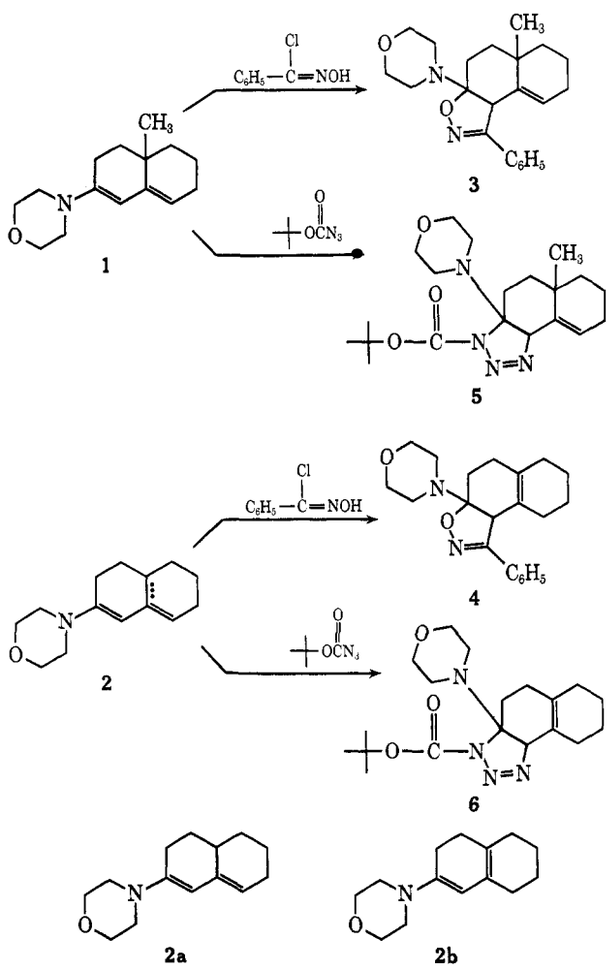
Terminal coupling of dienamines with aryldiazonium salts was found in dimethylformamide or water, while the use of dichloromethane or chloroform as solvent led to a mixture of α and γ coupling products.[43,44]



1,3-Dipolar Reactions.—The morpholine enamine derivatives of 10-methyl-$\Delta^{1(9)}$-2-octalone (**1**) and $\Delta^{1(9)}$-2-octalone (**2**) reacted with benzonitrile oxide, which was generated from the chloroxime by loss of hydrogen chloride, to give the aminoisoxazolines **3** and **4**. A nuclear magnetic resonance spectrum of **3** displayed a singlet at δ 3.8 for the isoxazoline proton and a triplet at δ 5.8 for the vinyl proton. Thus reaction at the amine substituted double bond of **1** was indicated. Lack of vinyl proton resonance in **4** again showed the same regiospecificity and indicated preferential reaction of the homoannular dienamine isomer **2b** in the mixture which contained predominantly the heteroannular dienamine isomer **2a**.

Similarly, *tert*-butyl azidoformate reacted with the

SCHEME I



dienamines **1** and **2** to give analogous adducts **5** and **6** (Scheme I). These products showed broad nmr signals at δ 4.8 and 4.6 for the heterocyclic protons and a broad vinyl signal at δ 5.5 for **5** but not for **6**.

Orientation of the 1,3-dipolar additions in **3** and **4** can be assigned from a comparison of chemical shifts of the heterocyclic protons in the two heterocyclic series and is consistent with other additions of nitrile oxides to enamines.[45] Direction of the acyl azide additions was assigned in analogy to other reactions of acyl and aryl azides with enamines.[46,47]

Attempts to obtain 1,3-dipolar additions of the preceding two 1,3-dipolar reagents to the ethyl enol ether and enol acetate derivatives of $\Delta^{1(9)}$-2-octalone and 10-methyl-$\Delta^{1(9)}$-octalone failed and led only to the isolation of 4,5-diphenylfuroxan when the nitrile oxide was used.

Methinylation Reaction.—The addition of diethylzinc and diiodomethane[48,49] to the dienamines **1** and **2** gave aminocyclopropane products **7** and **8** which showed cyclopropane protons at δ 0.2–1.0 and coupled vinyl proton signals at δ 5.4 in their nmr spectra. With a 50% excess of the carbenoid reagent only the monoaddition products to the nitrogen-substituted

(38) C. Jutz and W. Müller, *Chem. Ber.*, **100**, 1536 (1967).

(39) D. Burn, G. Cooley, M. Davies, J. W. Ducker, B. Ellis, P. Feather, A. K. Hiscock, D. Kirk, A. P. Leftwick, V. Petrow, and D. M. Williamson, *Tetrahedron*, **20**, 597 (1964).

(40) R. Sciaky, U. Pallini, and B. Patelli, *Gazz. Chim. Ital.*, **96**, 1268 (1964).

(41) R. Sciaky and F. Mancini, *Tetrahedron Lett.*, 137 (1965).

(42) Acylation at C-4 could be due to the homoannular diene in reaction of the 19-nor compounds.

(43) M. J. M. Pollmann, H. R. Reus, U. K. Pendit, and H. O. Huisman, *Recl. Trav. Chim. Pays-Bas*, **89**, 929 (1970).

(44) U. K. Pandit, M. J. M. Pollmann, and H. O. Huisman, *Chem. Commun.*, 527 (1969).

(45) M. E. Kuehne, S. J. Weaver, and P. Franz, *J. Org. Chem.*, **29**, 1582 (1964).

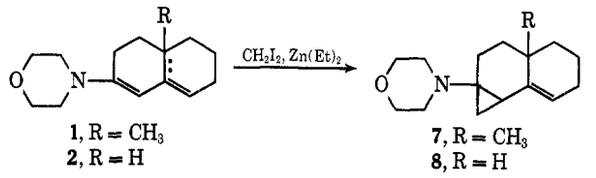
(46) Y. K. Kim and M. Munk, *J. Amer. Chem. Soc.*, **86**, 2213 (1964).

(47) E. Fanghaenel, *Z. Chem.*, **3**, 309 (1963).

(48) J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron*, **24**, 53 (1968).

(49) J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron Lett.*, 3495 (1968).

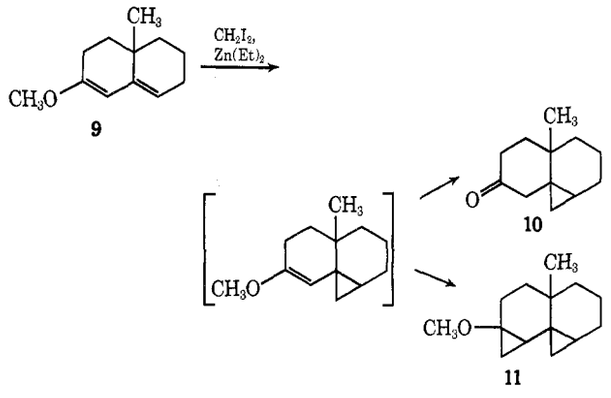
double bond were isolated. The reaction also appears to be stereospecific, at least in the addition to dienamine **1**, since there only one methyl signal could be detected in the total reaction product.



1, R = CH_3
2, R = H

7, R = CH_3
8, R = H

In contrast to these reactions, it was found that methylene groups were added preferentially to the terminal double bond of the methyldienol ether derivative **9** of 10-methyl-$\Delta^{1(9)}$-2-octalone. Thus the ketonic cyclopropane **10** and the dicyclopropane **11** were formed with a 50% excess of the methylene generating reagent. The dienol acetate derivative of the parent octalone was recovered unchanged under the same reaction conditions.

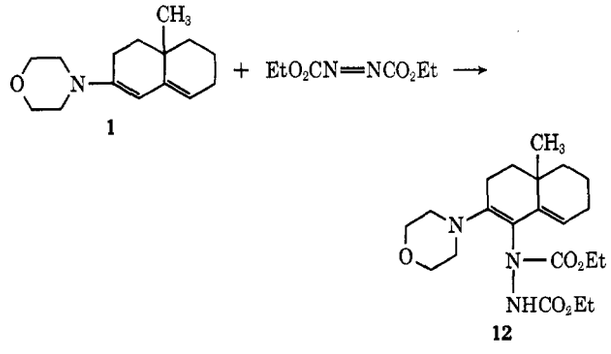


9

10

11

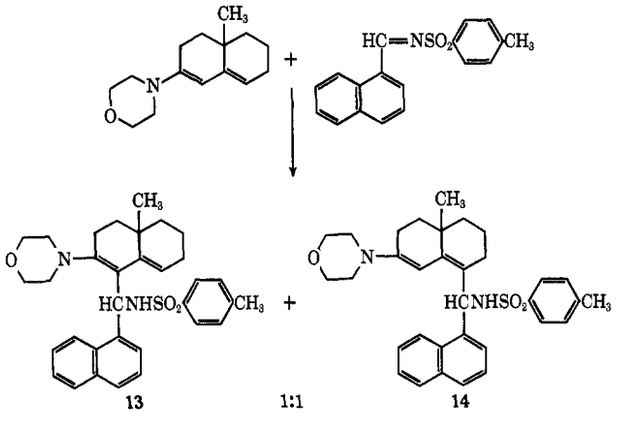
Reaction with Diethyl Azodicarboxylate.—The nitrogen-substituted double bond was also found to be substituted on addition of diethyl azodicarboxylate to the dienamine **1**. The nmr spectrum of the product **12** displayed a coupled vinyl proton. Addition of this reagent to the corresponding methyl dienol ether, however, resulted in reduction of the azo group and isolation of diethyl hydrazinedicarboxylate.



1

12

Reaction with 1-Naphthal-*p*-toluenesulfonimide.—In contrast to the foregoing dienamine reactions which were regiospecific for the nitrogen-substituted double bond, the reaction of **1** with a toluenesulfonimide[50] led to about equal addition to both double bonds. The product structures **13** and **14** could be assigned from observation of respective coupled and uncoupled vinyl protons, deuterium exchangeable sulfonamide protons, and conversion of the benzylic doublets to singlets on hydrogen–deuterium exchange. In product **13** the NH proton signal was quite diffuse, presumably because of hydrogen bonding to the morpholine nitrogen.



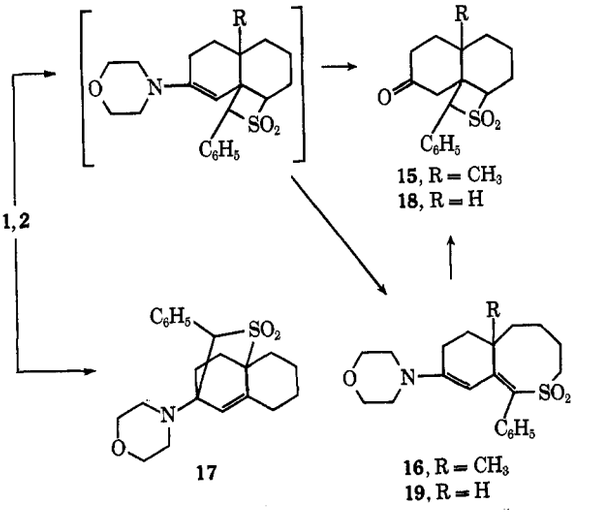
13 1:1 **14**

Reactions with Phenylsulfene.—The addition of benzylsulfonyl chloride to a mixture of the dienamine **1** and triethylamine resulted only in products of reaction at the end of the activated diene system. Thus hydrolytic work-up gave the tricyclic keto sulfone **15** and the ring expanded sulfone **16**. Heating of the reaction mixture in the absence of water and work-up resulted in the exclusive formation of **16** from the intermediate tricyclic enamine. On heating of **16** with aqueous acetic acid, the tricyclic keto sulfone **15** was formed. This interesting ring contraction may occur at the α,β-unsaturated imonium salt or the corresponding enone stage of the hydrolysis.

When benzyl sulfonyl chloride was added to the dienamine **2**, analogous products **18** and **19** were formed, as well as the bridged sulfone **17**, as major product.

Decreased medium basicity, which should allow direct sulfonation by the acid chloride, rather than initial sulfene generation, did not alter the course of these reactions. Thus identical products were obtained with or without triethylamine.

Attempts to add phenylsulfene to the enol ether derivative **9** of 10-methyl-$\Delta^{9(1)}$-2-octalone resulted only in the formation of stilbene in 46% yield. Stilbene was also formed from benzenesulfonyl chloride and triethylamine in petroleum ether.



15, R = CH_3
18, R = H

17

16, R = CH_3
19, R = H

(50) G. Kresze and R. Albrecht, *Angew. Chem.*, **74**, 781 (1962).

Experimental Section

Nmr spectra were recorded on a Varian A-60 instrument, ir spectra on a Perkin–Elmer 21 instrument, and uv spectra on a Perkin–Elmer 202 instrument. Melting points are corrected.

The preparations of 4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone, bp 78° (0.1 mm), 2,4-dinitrophenylhydrazone mp 171–172°, and its 4a-methyl analog, bp 100° (0.1 mm), semicarbazone mp 204–205, were carried out according to the method of Ross and Levine.[51] Conversion to the respective enamine derivatives **1**, bp 122–125° (0.6 mm), 67% yield, and **2**, bp 118–120° (0.5 mm), 62% yield, was achieved by azeotropic removal of water.[52] Compound **2** showed a 60:40 ratio of heteroannular to homoannular diene (nmr H-1 5.20 (s), H-8 5.30 (m) *vs.* H-1 (4.72), respectively). Using a procedure similar to one described,[53] 2-methoxy-3,4,4a,5,6,7-hexahydro-4a-methylnaphthalene (**9**) was obtained by solution of the parent octalone, 8.0 g (0.049 mol), and a few crystals of *p*-toluenesulfonic acid in 20 ml of a 3:1 mixture of methanol and dioxane. After 3 hr at room temperature 1.0 ml of triethylamine was added, the mixture concentrated under vacuum, and the enol ether distilled to give 6.50 g (71% yield): bp 78–80° (0.35 mm); ν_{max}^{neat} 1660 and 1620 cm^{-1}; nmr (neat) δ 0.83 (s, 3 H), 3.33 (s, 3 H), 4.97 (s, 1 H), and 5.05 (t, 1 H).

Anal. Calcd for $C_{13}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.56; H, 10.05.

Reactions of 2-(*N*-Morpholino)-3,4,4a,5,6,7-hexahydro-4a-methylnaphthalene (1) and 2-(*N*-Morpholino)-3,4,4a,5,6,7-hexahydronaphthalene (2) with Benzonitrile Oxide to 3 and 4.—A solution of 400 mg (2.58 mmol) of phenylhydroxamoyl chloride[54] in 10 ml of anhydrous benzene was added to 1.80 g (7.80 mmol) of the dienamine **1** or 1.70 g (7.80 mmol) of the dienamine **2**, in 10 ml of benzene, at 0°, under a nitrogen atmosphere. After 2 hr at 0° and 48 hr at room temperature, the solid amine hydrochlorides were filtered and the filtrates concentrated under vacuum. Addition of a little methanol and water, extraction with dichloromethane, concentration, and trituration with petroleum ether (bp 30–60°) gave 183 mg (20% yield) of **3**, mp 163–165°, and 330 mg (38% yield) of **4**, mp 185–188°. The products were recrystallized from methanol. **3** had mp 166–167°; ν_{max}^{KBr} 1460, 1440, and 1115 cm^{-1}; λ_{max}^{EtOH} 220 and 265 mμ; nmr ($CDCl_3$) δ 0.80 (s, 3 H), 2.67 (t, 4 H), 3.60 (t, 4 H), 3.80 (s, 1 H), 5.80 (t, 1 H), and 7.20–7.80 (m, 5 H).

Anal. Calcd for $C_{22}H_{26}N_2O_2$: C, 74.85; H, 7.98; N, 8.14. Found: C, 74.95; H, 8.01; N, 7.95.

4 had mp 193–194°; ν_{max}^{KBr} 1440 and 1115 cm^{-1}; λ_{max}^{EtOH} 220 and 260 mμ; nmr ($CDCl_3$) δ 2.70 (t, 4 H), 3.57 (t, 4 H), 3.73 (s, 1 H), and 7.20–7.80 (m, 5 H).

Anal. Calcd for $C_{21}H_{26}N_2O_2$: C, 74.50; H, 7.74; N, 8.27 Found: C, 74.21; H, 7.64; N, 8.41.

Reactions of Enamines 1 and 2 with *tert*-Butyl Azidoformate to 5 and 6.—A mixture of 651 mg (2.79 mmol) of dienamine **1** and 400 mg (3.80 mmol) of *tert*-butyl azidoformate was stored at room temperature, in the dark, under nitrogen, without solvent, for 56 hr. Trituration with pentane gave 240 mg (23% yield) of **5**, mp 123–126°. Recrystallization from pentane gave needles: mp 129–130°; ν_{max}^{KBr} 1708 cm^{-1}; λ_{max}^{EtOH} 250 mμ; nmr ($CDCl_3$) δ 1.20 (s, 3 H), 1.60 (s, 9 H), 2.50 (t, 4 H), 3.70 (t, 4 H), 4.82 (broad, 1 H), and 5.52 (broad, 1 H).

Anal. Calcd for $C_{20}H_{32}N_4O_3$: C, 63.80; H, 8.57; N, 14.88. Found: C, 64.05; H, 8.53; N, 14.90.

Using the same procedure with 1.07 g (4.88 mmol) of dienamine **2** and 700 mg (6.65 mmol) of *tert*-butyl azidoformate gave 797 mg (45% yield) of **6**, mp 104–106. Recrystallization from pentane gave needles: mp 105–106°; ν_{max}^{KBr} 1702 cm^{-1}; λ_{max}^{EtOH} 250 mμ; nmr ($CDCl_3$) δ 1.52 (s, 9 H), 2.50 (t, 4 H), 3.60 (t, 4 H), and 4.50 (broad, 1 H).

Anal. Calcd for $C_{19}H_{30}N_4O_3$: C, 62.95; H, 8.34; N, 15.46. Found: C, 63.25; H, 8.46; N, 15.69.

Reactions of Dienamines 1 and 2 with Diiodomethane and Diethylzinc to 7 and 8.—To a solution of 500 mg (2.14 mmol) of the dienamine **1** in 20 ml of benzene was added 0.5 ml of diethylzinc at 0°, under nitrogen. A solution of 0.25 ml (3.10 mmol) of diiodomethane in 10 ml of benzene was then added over 30 min. After an additional 0.5 hr at room temperature the reaction mixture was quenched with 50 ml of cold 25% ammonium hydroxide solution and extracted with two 50-ml portions of benzene. Concentration of the magnesium sulfate dried extracts and distillation at 75–78° (0.006 mm) gave 180 mg (34% yield) of **7**, mp 88–89°, which was recrystallized from petroleum ether without change of melting point: nmr ($CDCl_3$) δ 0.20–1.00 (m, 2 H), 1.00 (s, 3 H), 2.60 (t, 4 H), 3.55 (t, 4 H), and 5.40 (t, 1 H). The crude undistilled product showed only one methyl singlet at δ 1.00 as well.

Anal. Calcd for $C_{16}H_{25}NO$: C, 77.68; H, 10.19. Found: C, 77.31; H, 10.26.

Reaction of the dienamine **2** under the same conditions and on the same scale gave 180 mg (34% yield) of **8**, as a colorless oil: bp 75–80° (0.007 mm); nmr ($CDCl_3$) δ 0.40–1.00 (m, 2 H), 2.60 (t, 4 H), 3.50 (t, 4 H), and 5.40 (m, 1 H).

Anal. Calcd for $C_{15}H_{23}NO$: C, 77.20; H, 9.94; N, 6.00. Found: C, 77.45; H, 9.79; N, 6.22.

Reaction of 2-Methoxy-3,4,4a,5,6,7-hexahydro-4a-methylnaphthalene (9) with Diiodomethane and Diethylzinc to 10 and 11.—Following the preceding reaction procedure for the dienamines, but with a 12-hr reaction time, 500 mg (2.81 mmol) of the dienol ether **9** was converted to 230 mg (45% yield) of an oily product which gave an nmr spectrum with two methyl singlets of equal intensity at δ 1.10 and 0.94. Preparative plate chromatography on silica gel, with benzene, afforded two products. The faster moving ketone **10**, bp 45° (0.5 mm), was contaminated by olefinic material and showed ν_{max}^{neat} 1705 cm^{-1}; nmr (CCl_4) δ 0.2–0.9 (m, 3 H), 1.10 (s, 3 H), and 4.75 (d or unresolved q, <1 H).

The slower moving dicyclopropane **11**, bp 40–44° (0.01 mm), showed nmr (CCl_4) δ 0.00–0.86 (m, 6 H), 0.94 (s, 3 H), and 3.17 (s, 3 H).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.20; H, 10.50.

Reaction of Enamine 1 with Diethyl Azodicarboxylate to 12.—A solution of 274 mg (1.57 mmol) of diethyl azodicarboxylate in 10 ml of anhydrous tetrahydrofuran was added at 0°, under nitrogen, to 400 mg (1.71 mmol) of dienamine **1** during 20 min. After 2 hr at 0° and 24 hr at room temperature (reaction mixture changed from orange to pale yellow), the solution was concentrated under vacuum and chromatographed on 20 g of Florisil eluting with 5% ethyl acetate in benzene. The first 150 ml of eluent produced 270 mg (42% yield) of crystalline **12** after trituration with petroleum ether. The product, recrystallized from hexane, showed mp 113–115°; ν_{max}^{KBr} 3350, 1750, and 1690 cm^{-1}; λ_{max}^{EtOH} 278 mμ; nmr ($CDCl_3$) δ 1.01 (s, 3 H), 1.1–1.8 (m, 12 H), 2.20 (m, 4 H), 2.70 (t, 4 H), 3.70 (t, 4 H), 4.00–4.30 (m, 4 H), 6.30 (m, 1 H), and 7.67 (s, 1 H).

Anal. Calcd for $C_{21}H_{33}N_3O_5$: C, 61.89; H, 8.16; N, 10.31. Found: C, 61.63; H, 8.41; N, 10.01.

Reaction of Enamine 1 with 1-Naphthal-*p*-toluenesulfonimide to 13 and 14.—A benzene solution of 400 mg (1.71 mmol) of the dienamine **1** and 400 mg (1.30 mmol) of 1 naphthal-*p*-toluenesulfonimide[55] was refluxed under nitrogen for 24 hr and concentrated under vacuum. Trituration with an ether–cyclohexane mixture gave 570 mg (81%) of a mixture of **13** and **14**. The nmr spectrum of this product showed two aromatic methyl singlets at δ 2.37 and 2.40 of about equal intensity. Recrystallization from ethanol gave **13**: mp 171–172°; ν_{max}^{KBr} 3200, 1612, and 1587 cm^{-1}; λ_{max}^{EtOH} 233 and 298 mμ; nmr ($CDCl_3$) δ 0.97 (s, 3 H), 2.37 (s, 3 H), 3.10 (t, 4 H), 3.80 (t, 4 H), 5.50 (d, 1 H), 5.95 (s, 1 H), 6.45 (d, 1 H), and 7.00–8.00 (m, 11 H). Addition of one drop of D_2O resulted in loss of the signal at δ 5.50 (NH) and collapse of the signal at δ 6.45 (adjacent CH) to a broad singlet.

Anal. Calcd for $C_{33}H_{38}N_2O_3S$: C, 73.00; H, 7.05; N, 5.16; S, 5.90. Found: C, 72.91; H, 7.12; N, 5.08; S, 5.79.

Crystallization of the mother liquor material from methanol gave **14**: mp 164–165°; ν_{max}^{KBr} 3200, 1612, and 1587 cm^{-1}; λ_{max}^{EtOH} 240 and 290 mμ; nmr ($CDCl_3$) δ 0.97 (s, 3 H), 2.40 (s, 3 H), 2.90 (t, 4 H), 3.70 (t, 4 H), 5.00 (m, 1 H), 5.60 (b, 1 H), 6.45 (d, 1 H), and 7.00–8.00 (m, 11 H). Addition of one drop of D_2O changed the δ 6.45 signal to a singlet.

Anal. Calcd for $C_{33}H_{38}N_2O_3S$: C, 73.00; H, 7.05; N, 5.16; S, 5.90. Found: C, 72.83; H, 7.05; N, 5.03.

Reactions of Enamines 1 and 2 with Phenylsulfene. (a) **Dienamine 1.**—A solution of 500 mg (2.80 mmol) of benzylsul-

(51) N. Ross and R. Levine, *J. Org. Chem.*, **29**, 2341 (1964).

(52) G. Stork, A. Brizzolara, H. Landesman, J. Szmuskovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(53) R. Villotti, C. Djerassi, and H. Ringold, *ibid.*, **81**, 4566 (1959).

(54) A. Werner and H. Buss, *Ber.*, **27**, 2193 (1894).

(55) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4406 (1968).

fonyl chloride in 10 ml of dichloromethane was added to a solution of 620 mg (2.70 mmol) of the dienamine **1** and 1.0 ml of triethylamine in 20 ml of dichloromethane at −15°, under nitrogen. After 2 hr at −15° and 12 hr at room temperature, the mixture was extracted with 5% hydrochloric acid, dried over magnesium sulfate, filtered, and concentrated under vacuum. Addition of 1:1 ether–ethyl acetate caused crystallization of products **15** and **16**. The white solid **15**, 100 mg (13% yield), mp 242–244°, was recrystallized from ethyl acetate and methanol to mp 244–246°: ν_{max}^{KBr} 1700 cm^{-1}; λ_{max}^{EtOH} 225 mμ; nmr ($CDCl_3$) δ 1.10 (s, 3 H), 4.00 (m, 1 H), 5.50 (s, 1 H), and 7.30–7.70 (m, 5 H).

Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.92; H, 6.96; S, 10.06. Found: C, 67.82; H, 7.05; S, 10.33.

The yellow crystals of **16** were recrystallized from ethanol to give 200 mg (22% yield): mp 169–170°; ν_{max}^{KBr} 1570 cm^{-1}; λ_{max}^{EtOH} 226 and 393 mμ; nmr ($CDCl_3$) δ 1.04 (s, 3 H), 3.10 (t, 4 H), 3.65 (t, 4 H), 4.20 (m, 2 H), 6.22 (s, 1 H), and 7.30 (s, 5 H).

Anal. Calcd for $C_{22}H_{29}NO_3S$: C, 68.18; H, 7.54; N, 3.62; S, 8.28. Found: C, 68.18; H, 7.55; N, 3.65; S, 8.35.

An intermediate tricyclic enamine could be seen in the initial reaction product by ν_{max}^{neat} 1660 cm^{-1}. This absorption band was lost on hydrolysis or on heating. When the total reaction product mixture was heated for 2 hr at 80°, the ir spectrum changed to that of the ring expanded dienamine **16**. A solution of 50 mg of **16** in 30% aqueous acetic acid was heated at reflux for 1 hr. Extraction with dichloromethane and washing with aqueous sodium carbonate gave a crude product with ν_{max}^{film} 1660 and 1700 cm^{-1}. Trituration with ethyl acetate gave 25 mg (60% yield) of the ketone **15**.

(b) **Dienamine 2.**—This reaction was carried out without triethylamine. A solution of 880 mg (4.63 mmol) of benzylsulfonyl chloride in 10 ml of dichloromethane was added to 2.00 g (9.16 mmol) of dienamine **2** in 50 ml of dichloromethane at −20°, under nitrogen, during 1 hr. After 2 hr at this temperature and 10 hr at room temperature, the mixture was extracted with water; the organic phase was dried over magnesium sulfate and concentrated. Trituration with ethyl acetate gave three products: The bridged sulfone **17**, 350 mg (20% yield), mp 142–143°, was recrystallized from ethyl acetate and cyclohexane to mp 149–150°: ν_{max}^{KBr} 1450 cm^{-1}; λ_{max}^{EtOH} 215 mμ; nmr ($CDCl_3$) δ 1.5–2.9 (m, 16 H), 3.33 (m, 4 H), 4.52 (s, 1 H), 4.85 (s, 1 H), and 7.20–7.60 (m, 5 H).

Anal. Calcd for $C_{21}H_{27}NO_3S$: C, 67.27; H, 7.29; N, 3.75; S, 8.58. Found: C, 67.27; H, 7.48; N, 3.84; S, 8.98.

The keto sulfone **18**, 100 mg (7% yield), was recrystallized from ethanol to mp 232–233°: ν_{max}^{KBr} 1705 cm^{-1}; λ_{max}^{EtOH} 225 mμ; nmr ($CDCl_3$) δ 4.15 (m, 1 H), 5.10 (s, 1 H), and 7.40 (s, 5 H).

Anal. Calcd for $C_{17}H_{20}O_3S$: C, 67.07; H, 6.62; S, 10.53. Found: C, 66.88; H, 6.51; S, 10.36.

The dienamine sulfone **19**, 80 mg (4% yield), was recrystallized from ethyl acetate and showed ν_{max}^{KBr} 1575 cm^{-1}: nmr ($CDCl_3$) δ 3.15 (t, 4 H), 3.80 (t, 4 H), 4.30 (t, 2 H), 6.40 (s, 1 H), and 7.40–7.48 (d, 5 H).

Reaction of Phenylsulfene with Dienol Ether 9.—The reaction was carried out as described for method a used with the dienamines. Only *trans*-stilbene, mp 123° (46% yield), and recovered dienol ether **9** were isolated.

Registry No.—**1**, 23088-12-2; **2a**, 23088-05-3; **2b**, 23088-06-4; **3**, 33527-50-3; **4**, 33527-51-4; **5**, 33527-52-5; **6**, 33527-53-6; **7**, 33527-54-7; **8**, 33527-55-8; **9**, 33527-56-9; **10**, 33527-57-0; **11**, 33527-58-1; **12**, 33527-59-2; **13**, 33527-60-5; **14**, 33527-61-6; **15**, 33527-62-7; **16**, 33527-63-8; **17**, 33527-64-9; **18**, 33527-65-0; **19**, 33527-66-1; *trans*-stilbene, 103-30-0.

Organic Fluorine Compounds. XXXIII.[1] Electrophilic Additions to Fluoro Olefins in Superacids

GEORGE A. OLAH* AND Y. K. MO

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received August 23, 1971

A series of fluoro olefins (I–X) were studied in the superacid systems, SbF_5–HF–SO_2ClF, SbF_5–HSO_3F–SO_2ClF, or in HSO_3F at low temperature. Eight of the fluoro olefins (I–VIII) reacted with the acid systems to give the corresponding fluoride or fluorosulfonate addition products. A preparative method for preparation of α-fluoroethyl and α,α-difluoroethyl fluorosulfate in 90–95% yield was developed. No long-lived fluorocarbenium ion[2] intermediates were observed, even in these very low nucleophilicity acid systems, as they react rapidly with gegenions to give the observed covalent fluorides or fluorosulfates. Two of the fluoro olefins (IX and X) were found to be inert even in superacids. 1,1,1-Trihaloethanes, CH_3CX_3 (X = F and Cl), reacted with SbF_5–SO_2ClF at −80° to give the first stable methyldihalocarbenium ion, $CH_3C^+X_2$ (X = F and Cl).

Due to the high electronegativity of fluorine the replacement of hydrogen by fluorine in ethylene results in the withdrawal of electron density from the π-electron system. Consequently, most of the ionic reactions of fluoro olefins are due to nucleophilic attack. The ionic reactions of fluoro olefins have been reviewed by Chambers and Hobbs.[3] They concluded that electrophilic attack on fluoro olefins may only be achieved in the presence of strong Lewis acid catalyst. However, no direct evidence was provided for this assumption. With techniques developed in our laboratories for study of stable carbenium ions in superacids and for their low-temperature nuclear magnetic resonance spectroscopic study, we attempted the protonation of a series of fluoro olefins hoping to study their protolytic behaviors and thus directly observe, if possible, the related fluorocarbenium ion and to evaluate the possibility of ionic polymerization of fluoro olefins in superacids.

Results

Ten fluoro olefins ($R_1R_2C{=}CR_3R_4$) were selected for our studies (I–X). Two different superacid media with variable ratio of SbF_5–HF and SbF_5–HSO_3F in

$R_1R_2C{=}CR_3R_4$

I, $R_1 = R_2 = R_3 = H$; $R_4 = F$
II, $R_1 = R_2 = H$; $R_3 = R_4 = F$
III, $R_1 = R_3 = H$; $R_2 = R_4 = F$
IV, $R_1 = R_2 = R_3 = F$; $R_4 = H$
V, $R_1 = R_3 = H$; $R_2 = Cl$; $R_4 = F$
VI, $R_1 = R_2 = R_3 = F$; $R_4 = Cl$
VII, $R_1 = R_2 = R_3 = F$; $R_4 = Br$
VIII, $R_1 = R_2 = R_3 = F$; $R_4 = I$
IX, $R_1 = R_2 = R_3 = R_4 = F$
X, $R_1 = R_2 = R_3 = F$; $R_4 = CF_3$

(1) Part XXXII: G. A. Olah and Gh. Mateescu, *J. Amer. Chem. Soc.*, **93**, 781 (1971).

(2) For a discussion of the general concept of carbocations and differentiation of trivalent carbenium ion from penta- (or tetra-) coordinated carbonium ions, see G. A. Olah, *ibid.*, **94**, 808 (1972).

(3) R. D. Chambers and R. H. Mobbs in "Advances in Fluorine Chemistry," Vol. 4, M. Stacey, J. C. Tatlow, and A. G. Sharpe," Ed., Butterworths, London, 1965.